

(21) Application No 9102113.9

(22) Date of filing 31.01.1991

(71) Applicant  
Glaverbel

(Incorporated in Belgium)

Chaussee De La Hulpe 166, Watermael-Boltsfort,  
B-1170 Brussels, Belgium

(72) Inventors  
Robert Terneu  
Michel Hannotiau  
Karel Vandiest

(74) Agent and/or Address for Service  
Hyde, Heide & O'Donnell  
10-12 Priests Bridge, London, SW15 5JE,  
United Kingdom

(51) INT CL<sup>5</sup>  
C03C 17/25, C23C 18/12

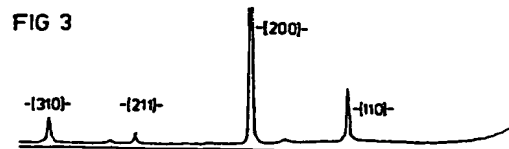
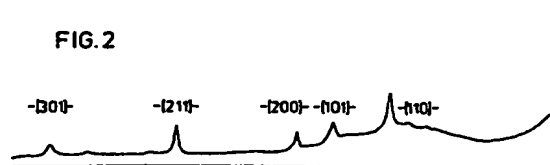
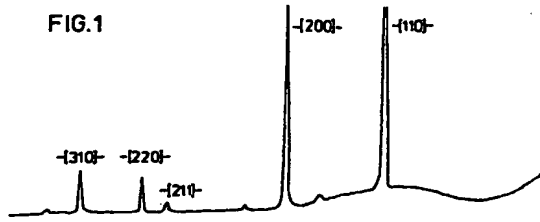
(52) UK CL (Edition K)  
C7F FHB FHD FQ914 FR909 FR914 F782  
U1S S2069

(56) Documents cited  
GB 2035979 A JP 730027726 B JP 620093804 A

(58) Field of search  
UK CL (Edition K) C7F FHB FHD FHE FHZ  
INT CL<sup>5</sup> C03C, C23C  
Online databases: WPI

(54) Glass coated with two tin oxide coatings

(57) To provide glass bearing a tin oxide based coating which is of low haze without depending on the use of special glass or specially treated glass, and which does not require the formation of a barrier layer of some other substance, a hot glass substrate is first contacted with an undercoating precursor material comprising a chlorine-free organo-tin compound, such as dibutyl tin diacetate or dibutyl tin monoxide, thereby pyrolytically to deposit an underlayer of tin oxide, whereafter that underlayer is pyrolytically overcoated with a second tin oxide layer using tin chloride, preferably stannous chloride as overcoating precursor material. Such a coating comprises undercoating and overcoating layers which are both formed from tin oxide, and which have different crystal structures, and/or different crystal orientations. Whereas a typical tin oxide coating formed from a stannous chloride precursor exhibits high X-ray scattering due to the  $\{110\}$ - crystallographic plane (the  $\{110\}$ - peak is some 3.3 times the height of the next highest peak, the  $\{200\}$ - peak in figure 1), and a typical coating formed from an organo-tin precursor exhibits no predominant scattering peak as shown in Figure 2, a two-layer coating respectively formed from organo-tin and tin chloride precursors may typically exhibit an intense peak due to scattering by the  $\{200\}$ - plane as shown in Figure 3.



At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

$\frac{1}{2}$

FIG. 1

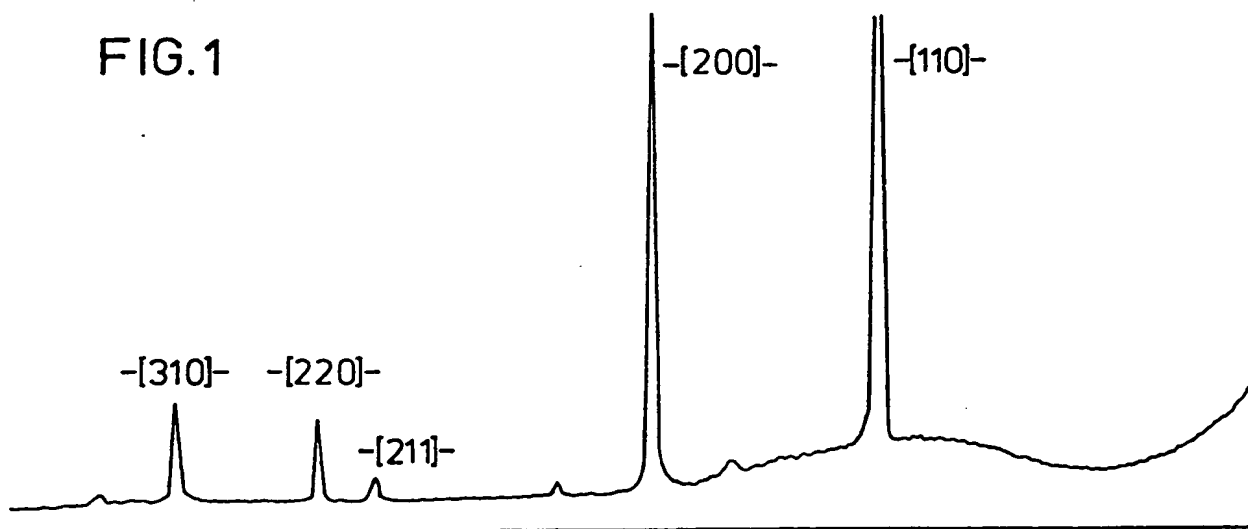


FIG. 2

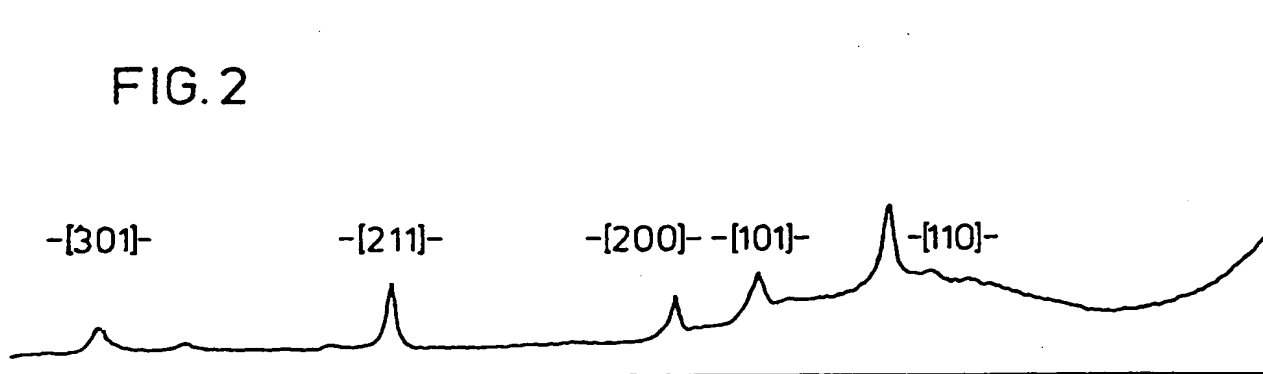
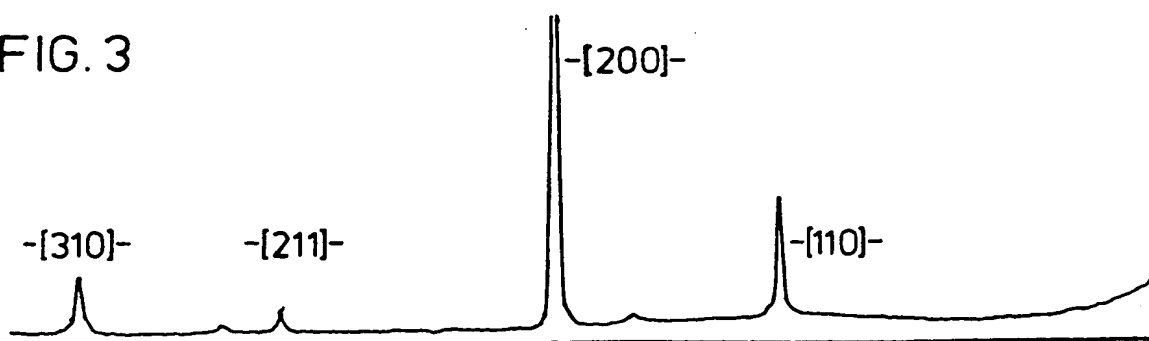


FIG. 3



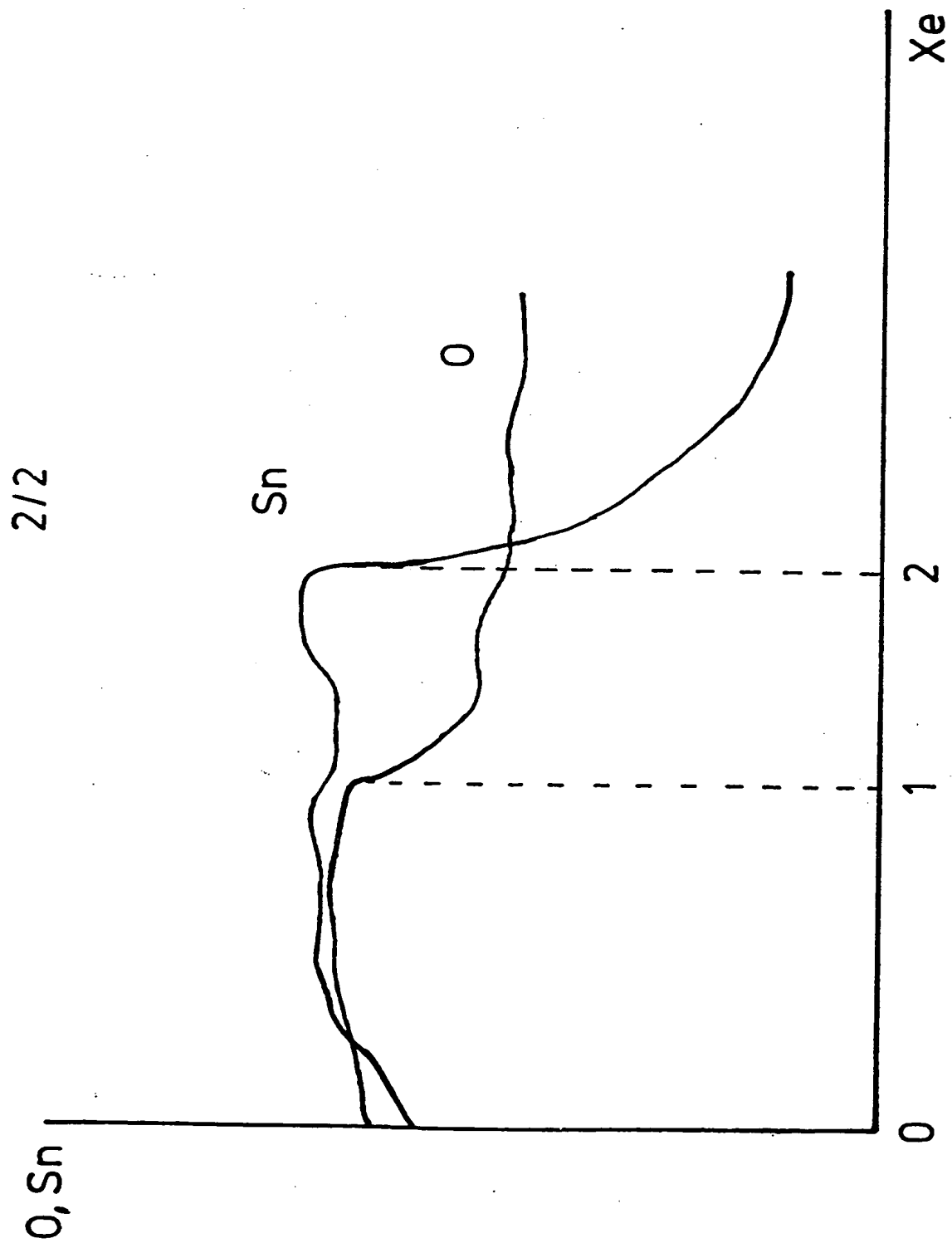


FIG.4

## TIN OXIDE COATED GLASS

This invention relates to glass bearing a transparent, pyrolytically formed coating comprising tin oxide, and to a process of pyrolytically forming a transparent tin oxide coating on a glass substrate.

5 The invention is particularly concerned with tin oxide coatings which are of moderate to high thickness, for example those having a thickness greater than 300 nm.

Glass bearing a transparent, pyrolytic tin oxide coating is well known. Such coatings may be provided simply in order to give an increased abrasion resistance to the substrate, or they may be applied in  
10 order to affect the electrical properties of the coated substrate, and/or its properties in relation to incident electromagnetic radiation. For example it is well known to provide sheet glass with a tin oxide coating which has been doped to render it conductive. Such coatings can have the property of reducing the emissivity of the coated face in respect of  
15 infra red radiation, especially infra red radiation having wavelengths greater than 3000 nm, and such coated sheets are widely used as window glazings. Such coatings may also be incorporated in electrical circuits of various kinds: as a very simple example, such a coating might be constituted as an electrical resistance heating element, or as a  
20 transparent electrode, for example for a display device or a photovoltaic cell.

In industrial production, such coatings are most often formed by the pyrolysis of tin chloride. It is usual to use stannous chloride as coating precursor material, though stannic chloride is sometimes used.  
25 The coating precursor material, whether in the form of vapour or a spray of a solution is caused to contact the glass substrate to be coated while the latter is hot, and the tin chloride undergoes pyrolytic reaction in contact with the substrate in order to form a stannic oxide coating *in situ*. The tin oxide coating has the crystalline form of cassiterite, that  
30 is to say it is of the holosymmetric class in the tetragonal system.

Glass coated in that way may be investigated by X-ray diffraction techniques in order to ascertain the internal structure of the coating. The result of such an investigation may be plotted as a continuous graph of the intensities of X-radiation which has been deflected through  
5 different angles. When such an investigation is made, it is found that there is a continuous background scattering which is substantially constant over a wide range of angles. This is due to the non-crystalline arrangement of atoms in the lattice of the glass substrate. Superimposed on that background scattering are found various peaks  
10 which correspond to different crystallographic planes in the coating, and the heights of those peaks above the background scattering level give an indication of the relative intensities of X-radiation scattered through various angles and thus of the relative occurrence of various crystallographic planes within the coating structure.

15 Figure 1 of the drawings hereof shows such a graph in respect of a typical coating of known type formed by spraying an aqueous solution of stannous chloride containing a doping precursor agent in order to form a coating 300 nm in thickness. It will be seen that that graph exhibits peaks which correspond to the following crystallographic  
20 planes:  $[-110]-$ ,  $[-200]-$ ,  $[-310]-$ , and  $[-220]-$ , with relatively minor peaks corresponding to the  $[-211]-$  plane, and to other planes. In fact the peak corresponding to the  $[-110]-$  plane, which is the highest or most intense peak, runs off the drawing with the scale used and it is about 3.3 times the height of the next highest peak, the  $[-200]-$  peak.  
25 The coating thus has a highly ordered structure, and the  $[-110]-$  peak may also be said to predominate in the sense that its height is greater than the combined heights of all other peaks.

In the case of tin oxide coated glass to be used as a window glazing, it will be appreciated that the transparency of the coating is of  
30 major importance. It is generally desirable that the coated glass should have a very low haze factor, that is, that the diffuse transmission of the coated glazing should be very low. Unfortunately, there is a problem

in the formation of tin oxide coatings with low haze on ordinary window glass, and this is believed to be due to undesired side reactions which take place during the coating process between coating reaction products and sodium ions within the glass.

5       According to current belief in the glass coating art, in the course of the coating process using a tin chloride as coating precursor material, chlorine ions may react directly or indirectly with sodium ions at the surface of the glass. The precise mechanism is not wholly clear, but the end result is the same: sodium chloride is formed. That sodium  
10       chloride may become incorporated into the tin oxide coating. Sodium chloride, of course, crystallizes in the cubic system. Because of the incorporation of sodium chloride in the tin oxide coating formed, the structure of that coating is irregular, and the coating exhibits haze.

15       A further disadvantage of the incorporation of sodium chloride in tin oxide coatings may be mentioned here, namely that sodium acts as a poison in certain kinds of electrical systems, such as liquid crystals, in which conductive tin oxide coatings may be used.

20       In order to overcome the disadvantage of incorporating sodium chloride in the tin oxide coating, many proposals have been made. It is for example known to make use of special alkali-free glasses, but this is very costly. It is also known to subject ordinary soda-lime window glass to a dealkalizing treatment in which sodium ions are leached out from surface layers of the glass prior to coating, but this is not always convenient, especially if the glass is to be coated while it is in the form  
25       of a continuous ribbon which is still hot from the manufacturing process, because dealkalization generally involves contacting the glass with an acid gas and then cleaning the glass prior to coating. It is also known to provide the glass with an undercoating of a relatively inert material such as silica or titanium dioxide which forms a barrier  
30       preventing the migration of sodium to the surface. The formation of a uniform oxide undercoating is itself not easy, and further difficulties may arise at the interface between such an undercoating and the tin

oxide coating. Also such oxide undercoatings tend to have a refractive index which is different both from the coated glass and from a tin oxide overcoating, and unless the thickness of that undercoating is very carefully controlled, this could give rise to interference effects which might render a window glazing commercially unacceptable.

Thus it will be seen that hitherto there has been no solution to the problem of forming a tin oxide coating of a moderate or high thickness on a glass substrate in a simple and economical manner so that the coating is substantially free from haze at the glass/coating interface. This is despite the length of time for which that problem has been known and despite the very considerable amount of time and effort which has been put towards finding such a solution.

It is an object of this invention to provide a process of pyrolytically forming a transparent, low haze, tin oxide coating on a hot glass substrate which is simple to perform and which is less costly to perform than previously known processes for producing coated glass exhibiting similarly low haze.

According to the present invention, there is provided a process of pyrolytically forming a transparent tin oxide coating on a hot glass substrate, characterized in that the hot glass substrate is first contacted with an undercoating precursor material comprising a chlorine-free organo-tin compound, thereby pyrolytically to deposit an underlayer of tin oxide, whereafter that underlayer is pyrolytically overcoated with a second tin oxide layer using tin chloride as overcoating precursor material.

The process of the invention is relatively easy to perform, and because of the absence of chlorine in the precursor used for forming the tin oxide underlayer, that underlayer is free from sodium chloride, and furthermore, that underlayer serves as a barrier substantially preventing interaction between sodium from the glass and chlorine or chlorine containing reaction products during formation of the overcoating layer. In the result, the coating is substantially free from haze due to

the incorporation of sodium chloride in the coating.

Furthermore, by virtue of the use of tin chloride as precursor material for the overcoating layer, the thickness of that layer, and thus of the total coating, can be built up rapidly. Tin chlorides are  
5 inexpensive in comparison with organo-tin compounds, they are readily soluble in water so that they may be sprayed in aqueous solution, and they favour higher coating thickness build up rates than organo-tin compounds. Also, we have found it relatively easier to incorporate doping ions in coating layers formed using a tin chloride as coating  
10 precursor.

The invention thus provides a process of producing glass bearing a tin oxide based coating which is of low haze without depending on the use of special glass or specially treated glass, and which does not require the formation of a barrier layer of some other substance.

15 Also, because the two coating layers are both of tin oxide, no problems arise at the coating layer interface, and in particular, the underlayer formed using a chlorine-free organo-tin compound will have the same refractive index as the upper coating layer formed from tin chloride so there will be no interference effects due to the presence of  
20 coating layers having different refractive indices, and thus the thickness of the underlayer, or variations in its thickness, are not of critical importance for the optical properties of the coated glass.

Also, because the two coating layers are both of tin oxide, the second layer keys securely to the first. Accordingly the coating is also  
25 hard and durable.

A coating formed by the process of the invention as defined above has a novel structure, and coatings of that structure are themselves useful as abrasion resistant, optionally conductive, coatings.

Accordingly in its second aspect, the present invention provides  
30 glass bearing a transparent, pyrolytically formed coating comprising tin oxide, characterised in that such coating comprises at least two layers (hereinafter called respectively the "undercoating and overcoating



layers") which are both formed from tin oxide, and which have different crystal structures, and/or different crystal orientations, and wherein at least the undercoating layer is substantially free from haze-inducing chlorine ions.

- 5        Such a coating is substantially free from haze at the glass/coating interface, and it is hard and durable. Such a coating can be made economically, and it can be formed by the process of the invention.

10        In preferred embodiments of the invention, the undercoating layer has a crystal structure such that X-ray diffraction monitoring reveals a scattering peak due to the presence of crystallographic planes of the -[110]- orientation which has a height less than the sum of the heights of the peaks due to X-ray scattering from all differently oriented crystallographic planes. We have found that this is a characteristic of coatings formed from chlorine-free organo-tin precursor materials.

- 15        It has not been found possible to investigate the X-ray diffraction pattern of an undercoating layer while it is overcoated. Accordingly, such investigation must be made on a specimen of glass which has been given the undercoating layer but has not yet been overcoated to form a product in accordance with the invention, or alternatively on a product of the invention after the overcoating layer has been removed. The overcoating layer can be removed by abrasion. Removal of the overcoating layer is facilitated if the thickness of that layer is known.

20        The thickness of the overcoating layer will usually be known, at least approximately, by the manufacturer, but it can also be estimated by Secondary Ion Mass Spectroscopy ("SIMS"), because the two different coating layers behave differently when subjected to heavy ion bombardment. If a specimen of glass coated with tin oxide is bombarded with Xenon ions, various ions from the coating and from the glass will be ejected. The manner in which they are ejected will depend on the depth at which they were located. The quantity of ejected ions of a given element can be plotted on a graph against the total quantity of the Xenon ions injected, and this corresponds with a scale of depth beneath the surface.

When this is done, there will be in the case of tin ions, as would be expected, an abrupt drop in tin ion intensity at the boundary between the coating and the glass. Compared with drawn glass, this drop in tin ion intensity may not be as steep in the case of float glass (which will have  
5 been floated along the surface of a bath of molten tin during manufacture) because some tin may have migrated into surface layers of the glass. It is nevertheless quite clear from inspection of a graph of the intensity of tin ion ejection where the coating ends and the glass begins.

10 The boundary between the two layers may be determined equally easily by inspection of a similar graph relating to the intensity of oxygen ion ejection. It seems that oxygen ions are ejected more easily from a coating formed using a tin chloride precursor than they are from a coating formed from a chlorine-free organo-tin precursor or indeed  
15 from the glass, and there is a noticeable step in the oxygen intensity graph at the boundary between the two coating layers, but very little change at the boundary between the undercoating and the glass.

Thus the relative thicknesses of the two coating layers may be estimated by a SIMS technique, and an appropriate proportion of the  
20 total coating may be abraded away to reveal the undercoating for X-ray diffraction analysis. The total thickness of the coating may be ascertained using a betascope.

In preferred embodiments of the invention, the undercoating layer has a crystal structure such that X-ray diffraction monitoring reveals no  
25 predominant scattering peak. Such a diffraction pattern is quite different from that revealed by investigation of any tin oxide coating layer which has been formed using a chlorine-containing coating precursor material.

Figure 2 of the accompanying drawings is a graph of the  
30 intensities of X-rays scattered through various angles by a glass substrate coated to a thickness of 300 nm using dibutyl tin diacetate as coating precursor material, and it is to the same vertical scale as the

graph constituting Figure 1. Such coating corresponds with one possible undercoating layer of the present invention. It will be seen that the structure of the coating is quite different from that represented in Figure 1. The heights of the most intense peaks in Figure 2 are very  
5 much less than the heights of the most intense peaks in Figure 1. Also, the ratios of the heights of the principal peaks revealed in Figure 2 are much closer to unity than are the ratios of the heights of the principal peaks revealed in Figure 1. Thus, while there are quite clear preferential orientations of crystallographic planes in a coating formed  
10 from tin chloride, there is little or no preferential crystallographic orientation in a coating formed from the chlorine-free organo-tin compound.

Preferred embodiments of the invention alternatively, or in addition, have the feature that the tin oxide coating as a whole has a  
15 crystal structure such that X-ray diffraction monitoring reveals a scattering peak due to the presence of crystallographic planes of the  $[-110]$ -orientation which has a height less than the sum of the heights of the peaks due to X-ray scattering from all differently oriented crystallographic planes. The tin oxide coating as a whole may give rise  
20 to at least one X-ray scattering peak which has a greater height than the scattering peak due to the presence of crystallographic planes of the  $[-110]$ -orientation, and in particular, such coating may have a crystal structure such that X-ray diffraction monitoring reveals a scattering peak due to the presence of crystallographic planes of the  $[-200]$ -  
25 orientation which has a height greater than the sum of the heights of the peaks due to X-ray scattering from all differently oriented crystallographic planes.

Such coating structures are not to be expected, as they require that the usual crystallographic structure and/or crystallographic orientation  
30 of a coating formed from tin chloride is substantially modified by the presence of the undercoating layer. This is illustrated by Figure 3 of the accompanying drawings which is a graph of X-ray diffraction

intensities of a typical coating formed in accordance with the invention. The specific coating whose diffraction pattern is shown in Figure 3 had a total thickness of 650 nm and was constituted by an overcoating layer formed from stannous chloride and doping agent as precursor material (compare Figure 1) and an undercoating layer  
5 formed from dibutyl tin diacetate as coating precursor material (compare Figure 2). The scales of Figures 1 and 2 are the same, while the vertical scale of Figure 3 is one fifth that of the other two figures.

The undercoating precursor material is advantageously selected  
10 from: dibutyl tin diacetate and dibutyl tin monoxide. Such materials are readily available at reasonable cost, and they may be caused to undergo pyrolytic reaction to deposit a tin oxide coating without difficulty.

Preferably, said overcoating precursor material comprises  
15 stannous chloride. Stannous chloride is available as an inexpensive coating precursor material, it is readily soluble in water, and it can be caused to react pyrolytically to give a very rapid rate of build up in thickness of a tin oxide coating.

Advantageously, at least the tin oxide overcoating layer contains  
20 doping ions. The coating may thus be rendered conductive so that it may be incorporated into an electrical circuit, for example as a resistance heating element or as an electrode of an electro-optical device, and/or so that it may be effective to reduce the emissivity of the coated glass surface in respect of infra-red radiation.

In preferred embodiments, the tin oxide overcoating layer contains  
25 a greater proportion of doping ions than the undercoating layer. We have found that the yield of doping ions is greater in the overcoating layer than in the undercoating layer, and the adoption of this feature accordingly promotes economic use of doping precursor material. For  
30 greatest economy, no doping agent is added to the undercoating precursor material.

The presence of doping ions in the overcoating layer may readily be ensured by providing that said overcoating precursor material includes at least one additive selected to give rise to the presence of doping ions in the resulting overcoating, as is preferred.

5        Preferably, the tin oxide undercoating layer is at least 140 nm in thickness. We have found that such thicknesses are ample to provide an effective barrier against reaction between the glass and any reaction products of the coating precursor used to form the overcoating layer.

Advantageously, the tin oxide undercoating layer is not more than  
10    350 nm in thickness. Limiting the thickness of the undercoating layer in this manner gives economic benefits since, (a) the undercoating precursor material is more expensive than the overcoating precursor material, and (b) the rate of coating thickness build up and the specific yield of coating is greater when using a tin chloride than when using an  
15    organo-tin compound, so that for a given total coating thickness, the total cost of the coating precursor materials used will be reduced.

Preferably, the tin oxide undercoating layer is thinner than the tin oxide overcoating layer. This has economic benefits as aforesaid, and also, increasing the thickness of the overcoating layer at the expense of  
20    the undercoating layer also makes it easier to incorporate doping ions in the coating to achieve good electrical conductivity.

Preferably, the tin oxide undercoating and overcoating layers together have a thickness of at least 500 nm in order to permit the achievement of good conductivity and/or low infra red emissivity.  
25    More preferably, the total coating thickness is at least 750 nm. This reduces interference effects due to the presence of the coating, and in particular it militates against iridization effects due to differential interference across a coated panel where there are unavoidable variations in the thickness of the total coating applied.

30    Advantageously, total diffuse light transmission through the coated glass is not more than 1.5 %, and preferably not more than 1 %. This promotes clear vision through the glass.

Preferably, said coating imparts to the coated face an emissivity in respect of infra-red radiation having wavelengths greater than 3000 nm which is less than 0.3 and is preferably less than 0.2. Such coatings form effective barriers against the transmission of infra red radiation from low temperature sources while allowing passage of solar infra red radiation. This is useful when the glass is in sheet form since heat loss from buildings such as dwelling places, offices and greenhouses may be reduced by glazing such buildings with such coated sheet glass.

Advantageously, both coating layers are formed from coating precursor material in the liquid phase. This is found most convenient to put into practice.

Preferably, the undercoating precursor material is dissolved in a solvent selected from one or more of dimethyl formamide, acetic acid, ethyl acetate. This is found to have a favourable effect on the formation of the undercoating layer.

The invention will now be described by way of example, and with reference to the accompanying drawings in which:

Figure 1 is a graph showing an X-ray diffraction pattern obtained by irradiation of a tin oxide coating deposited from a stannous chloride coating precursor material,

Figure 2 is a graph showing an X-ray diffraction pattern obtained by irradiation of a tin oxide coating deposited from an organo-tin coating precursor material,

Figure 3 is a graph showing an X-ray diffraction pattern obtained by irradiation of a two-layer tin oxide coating deposited in accordance with this invention, and

Figure 4 is a graph obtained by Secondary Ion Mass Spectroscopy ("SIMS"), illustrating the intensity of ejection of oxygen and tin against the intensity of heavy ion (xenon) bombardment.

Two coating stations are located in succession between the exit from a float glass chamber in which a continuous glass ribbon is formed on a bath of molten tin and a horizontal annealinglehr through which

that ribbon is passed before it is cut into sheets. Each coating station comprises a spray gun mounted for to and fro movement across the path of advance of the ribbon, and an aspirator for drawing off coating reactions products and unused coating precursor material. An optional  
5 radiant heater is placed above the path of the ribbon between the two coating stations to compensate for any heat loss or temperature inequalities in the ribbon due to the energy taken up by the coating reactions which take place in the first coating station where the undercoat is deposited.

10       EXAMPLE 1

In a specific practical example, for forming the undercoat, a solution is made up of dimethyl formamide containing dibutyl tin diacetate in an amount of 50% by volume. This solution is sprayed through a reciprocating spray head to contact the travelling ribbon of  
15 hot glass while its temperature is in excess of 550°C in order to form *in situ* a tin oxide undercoating layer 200 nm in thickness.

The undercoated ribbon substrate then passes beneath the radiant heater and into the second coating station where the overcoating layer of tin oxide is formed in a manner known *per se*, by spraying an  
20 aqueous solution of stannous chloride containing ammonium bifluoride (for the provision of doping ions in the coating) to form an overcoating layer 450 nm in thickness to give a total coating thickness of 650 nm.

The resulting coating has a uniform greenish yellow tint in reflection. Haze is measured as 1% diffuse transmission. The haze is  
25 substantially uniform and continuous over the area of the coating and it is accordingly barely visually perceptible. The emissivity of the tin oxide coating in respect of infra-red radiation having wavelengths greater than 3000 nm is 0.18 and the total visible light transmission of the coated glass sheet (6 mm in thickness) is 73 to 74%. The coating is  
30 hard and durable.

## COMPARATIVE TEST

A classical doped tin oxide coating is formed on 6 mm float glass to a thickness of 650 nm on a glass sheet. That coating is greenish yellow in reflection and has an emissivity of about 0.18 and the coated sheet has a luminous transmissivity of 75 to 76%. The coating exhibits an average of 2% haze, but that haze is variable over the area of the coating, thus detracting from the quality of the product and rendering the haze more easily perceptible visually.

### EXAMPLE 2.

In a variant of Example 1, the undercoating layer was formed to a thickness of 300 nm and the overcoating layer was formed to a thickness of 350 nm, thus retaining the same total coating thickness of 650 nm. That coating was again greenish yellow in reflection and it had an emissivity of about 0.2. The coated sheet had a luminous transmissivity of 73 to 74%. The coating exhibited a haze of about 0.7% and this was uniform across the coated area.

The structure of the coating on the glass is investigated by Secondary Ion Mass Spectroscopy (Figure 4), and by X-ray diffraction (Figure 3).

In the SIMS investigation, the coated glass is subjected to bombardment by xenon ions and the intensity of tin and oxygen atoms ejected is monitored. The results are normalised and smoothed and plotted, to different scales, along the ordinate of Figure 4, against the total xenon dose plotted along the abscissa, to give the curves shown on the graph which thus represents the relative intensities at which the respective tin and oxygen atoms are ejected from various depths beneath the surface of the overcoating layer.

It will be seen from the graph that there is an abrupt drop in the intensity of oxygen atoms emitted beginning at the dotted line indicated at 1. The depth beneath the surface of the overcoating layer corresponding to xenon bombardment intensities over the range 0 to 1 is therefore taken to be the thickness of the overcoating layer.



At dotted line 2, there is an abrupt drop in the intensity of tin atoms ejected. The undercoating layer is taken to occupy the depth range corresponding to xenon bombardment intensities over the range 1 to 2.

5 It is possible that the ejection of tin from depths corresponding to xenon bombardment intensities greater than 2 (that is, from the glass substrate) may be due to tin being pushed into the glass by the xenon bombardment, but it may be more likely that a certain amount of tin had diffused into the glass while it was being processed in the float chamber.

10 SIMS investigation thus enables a determination of the relative thicknesses of the two layers of the tin oxide coating.

The crystallographic structure of the coating as a whole may be investigated by an X-ray diffraction technique, and the intensities of X-rays diffracted through increasing angles are shown in Figure 3.

15 In Figure 3, as in Figures 1 and 2, the horizontal scale represents the angle of deflection of the diffracted X-rays, and the vertical scale the intensity of the X-radiation at various angles of deflection. The apparatus used was a SIEMENS (Trade Mark) D501 X-ray apparatus supplied at 40 kV and 30mA. Detection was by scintillometer, and the  
20 radiation, of wavelength 0.15409 nm (copper K alpha radiation), was filtered using a standard nickel filter.

The X-ray diffraction pattern of Figure 3 for a two layer coating in accordance with this Example may be compared and contrasted with X-ray diffraction patterns shown in Figures 1 and 2 which are each  
25 obtained from a glass substrate bearing a single layer tin oxide coating.

In Figure 1 is shown the result of testing a single layer coating of tin oxide formed by spraying an aqueous solution of stannous chloride containing a doping precursor agent in order to form a coating 300 nm in thickness. It will be seen that that graph exhibits peaks above a  
30 background level of diffraction which correspond to the following crystallographic planes:  $-[110]-$ ,  $-[200]-$ ,  $-[310]-$ , and  $-[220]-$ , with relatively minor peaks corresponding to the  $-[211]-$  plane, and to other planes.

The background diffraction is due to diffraction by the glass substrate, and it will be noted, as would be expected from a supercooled liquid, i.e. a non-crystalline structure, that the level of the background is more or less constant except at the right hand side of the drawing where that background rises as the angle of deflection approaches zero.

In fact the peak corresponding to the  $[-110]$ - plane runs off the drawing with the scale used and it is about 3.3 times the height of the  $[-200]$ - peak. The coating thus has a highly ordered structure, and the  $[-110]$ - peak may be said to predominate in the sense that its height is greater than the combined heights of all other peaks.

This result is typical of those obtained by testing coatings formed directly onto a glass substrate using stannous chloride as precursor material.

Figure 2 of the accompanying drawings, which is to the same vertical scale as that used in Figure 1, is a graph of the intensities of X-rays scattered through various angles by a glass substrate coated to a thickness of 300 nm using dibutyl tin diacetate as coating precursor material. The coating whose X-ray diffraction pattern is shown in Figure 2 thus corresponds to the undercoating layer of the two-layer coating of this Example, and whose X-ray diffraction pattern is shown in Figure 3. It will be seen that the coating structure represented in Figure 2 is rather different from that represented in Figure 1, and in particular that the  $[-110]$ - peak is approximately the same height above the background diffraction as the  $[-211]$ - peak, these being the two greatest peaks revealed. Also, the heights of the most intense peaks in Figure 2 are very much less than the heights of the most intense peaks in Figure 1. Other, smaller diffraction peaks corresponding to the  $[-101]$ -,  $[-200]$ -, and  $[-301]$ - peaks are also revealed.

In the diffraction pattern of Figure 3, it will also be noted that a number of peaks occur. However, these peaks do not, surprisingly, correspond to an averaging or summation of the peaks revealed in Figures 1 and 2. The peaks shown in Figure 3 correspond, in order of

decreasing intensity, to diffraction by the  $[-200]$ - plane, the  $[-110]$ - plane, the  $[-310]$ - plane, and the  $[-211]$ - plane, as indicated in the drawing. In fact on the vertical scale used, which is one-fifth of the scale of Figures 1 and 2, there is not room to show the full height of the  $[-200]$ - peak which is some 4 times the height of the  $[-110]$ - peak. Barely perceptible against background diffraction are peaks corresponding to diffraction at the  $[-101]$ - peak and the  $[-220]$ - peak (not referenced).

A further important indicator of the crystallographic structure of a coating or coating layer is the ratio of the height of a peak, especially the most intense peak, to the width of that peak at its mid-height. In Figure 3, the most intense peak is the  $[-200]$ - peak and its height/mid-height width ratio is approximately 8.5 units of intensity per milli-degree. The next most intense peak is the  $[-110]$ - peak and its height/mid-height width ratio is approximately 3.2 units of intensity per milli-degree. This clearly indicates that the  $[-200]$ - crystallographic plane is the preferential orientation in the structure of the coating.

While no direct comparison can be made with the structures revealed in Figures 1 and 2 because of the considerable difference between the thicknesses of those coatings and the coating whose structure is revealed in Figure 3, it may be noted that in the  $[-110]$ - peak, the most intense shown in Figure 1, this ratio is about 8.25 units of intensity per milli-degree, whereas in the  $[-110]$ - peak shown in Figure 2, that ratio is only about 0.16 units of intensity per milli-degree.

Thus, it will be seen that the structure of the coating is quite different from that represented in either Figure 1 or Figure 2. There is a quite clear preferential orientation of crystallographic planes in the two layer coating, but this is in the  $[-200]$ - plane, and not mainly in the  $[-110]$ - plane, due to the effect of the undercoating layer of tin oxide formed from dibutyl tin diacetate.

### EXAMPLE 3

A tin oxide undercoating layer was formed of 6 mm float glass to a thickness of 225 nm using a precursor solution of dimethyl formamide containing 25% by volume of dibutyl tin diacetate. A doped tin oxide  
5 overcoating layer was formed on top of that undercoating layer to a thickness of 535 nm using an aqueous solution of stannous chloride. The tin oxide coating thus had a total thickness of 760 nm.

The coating had an infra red emissivity of 0.18, and a neutral tint in reflection. The coated glass had a luminous transmissivity of 74 to  
10 75%. The coating exhibited a haze of 1% and this was uniform across the coated area.

Such a coated sheet may be compared with one which is coated in a classical manner with a single layer coating, 760 nm thick, of doped tin oxide formed using stannous chloride as precursor. Such a coating  
15 also has an infra red emissivity of about 0.18, and a neutral tint in reflection. The coated glass has a luminous transmissivity of 75 to 76%. However, the coating exhibits an average haze of 2% and this is not uniform across the coated area. Such haze varies from 1.5% to 2.5%, and it is very much more clearly visible.

**CLAIMS**

1. Glass bearing a transparent, pyrolytically formed coating comprising tin oxide, characterised in that such coating comprises at least two layers (hereinafter called respectively the "undercoating and overcoating layers") which are both formed from tin oxide, and which  
5 have different crystal structures, and/or different crystal orientations, and wherein at least the undercoating layer is substantially free from haze-inducing chlorine ions.
2. Coated glass according to claim 1, wherein the undercoating layer has a crystal structure such that X-ray diffraction monitoring  
10 reveals a scattering peak due to the presence of crystallographic planes of the  $[-110]$ - orientation which has a height less than the sum of the heights of the peaks due to X-ray scattering from all differently oriented crystallographic planes.
3. Coated glass according to claim 2, wherein the undercoating  
15 layer has a crystal structure such that X-ray diffraction monitoring reveals no predominant scattering peak.
4. Coated glass according to any preceding claim, wherein the tin oxide coating as a whole has a crystal structure such that X-ray diffraction monitoring reveals a scattering peak due to the presence of  
20 crystallographic planes of the  $[-110]$ - orientation which has a height less than the sum of the heights of the peaks due to X-ray scattering from all differently oriented crystallographic planes.
5. Coated glass according to claim 4, wherein the tin oxide coating as a whole gives rise to at least one X-ray scattering peak which  
25 has a greater height than the scattering peak due to the presence of crystallographic planes of the  $[-110]$ - orientation.
6. Coated glass according to claim 5, wherein the tin oxide coating as a whole has a crystal structure such that X-ray diffraction monitoring reveals a scattering peak due to the presence of  
30 crystallographic planes of the  $[-200]$ - orientation which has a greater height than any other peak due to X-ray scattering from any differently oriented crystallographic plane.

7. Coated glass according to claim 6, wherein the tin oxide coating as a whole has a crystal structure such that X-ray diffraction monitoring reveals a scattering peak due to the presence of crystallographic planes of the  $-[200]$ - orientation which has a height  
5 greater than the sum of the heights of the peaks due to X-ray scattering from all differently oriented crystallographic planes.

8. Coated glass according to any preceding claim, wherein at least the tin oxide overcoating layer contains doping ions.

9. Coated glass according to claim 8, wherein the tin oxide  
10 overcoating layer contains a greater proportion of doping ions than the undercoating layer.

10. Coated glass according to any preceding claim, wherein the tin oxide undercoating layer is at least 140 nm in thickness.

11. Coated glass according to any preceding claim, wherein the  
15 tin oxide undercoating layer is not more than 350 nm in thickness.

12. Coated glass according to any preceding claim, wherein the tin oxide undercoating layer is thinner than the tin oxide overcoating layer.

13. Coated glass according to any preceding claim, wherein the  
20 tin oxide undercoating and overcoating layers together have a thickness of at least 500 nm.

14. Coated glass according to any preceding claim, wherein total diffuse light transmission through the coated glass is not more than 1.5 %, and preferably not more than 1 %.

25 15. Coated glass according to any preceding claim, wherein said coating imparts to the coated face an emissivity in respect of infra-red radiation having wavelengths greater than 3000 nm which is less than 0.3 and is preferably less than 0.2.

16. A process of pyrolytically forming a transparent tin oxide coating on a hot glass substrate, characterized in that the hot glass substrate is first contacted with an undercoating precursor material comprising a chlorine-free organo-tin compound, thereby pyrolytically  
5 to deposit an underlayer of tin oxide, whereafter that underlayer is pyrolytically overcoated with a second tin oxide layer using tin chloride as overcoating precursor material.

17. A process according to claim 16, wherein said undercoating precursor material is selected from: dibutyl tin diacetate and dibutyl tin  
10 monoxide.

18. A process according to claim 16 or 17, wherein said overcoating precursor material comprises stannous chloride.

19. A process according to any of claims 16 to 18, wherein said overcoating precursor material includes at least one additive selected to  
15 give rise to the presence of doping ions in the resulting overcoating.

20. A process according to any of claims 16 to 19, wherein both coating layers are formed from coating precursor material in the liquid phase.

21. A process according to claim 20, wherein the undercoating  
20 precursor material is dissolved in a solvent selected from one or more of dimethyl formamide, acetic acid, ethyl acetate.

-21-

**Patents Act 1977**  
**Examiner's report to the Comptroller under**  
**Section 17 (The Search Report)**

Application number

9102113.9

**Relevant Technical fields**

(i) UK CI (Edition K ) C7F (FHB, FHD, FHE, FHZ)

(ii) Int CI (Edition 5 ) C23C; C03C

**Databases (see over)**

(i) UK Patent Office

(ii)

ONLINE DATABASES : WPI

**Search Examiner**

P G BEDDOE

**Date of Search**

26.3.91

Documents considered relevant following a search in respect of claims

1-21

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 2035979 A (CARL-ZEISS) see especially Claim 1 and Exs	1-17, 19,20
X	JP 730027726 B (GLAVERBEL) see English language abstract (WPI Acc No:70-30204R/18)	1
X	JP 620093804 A (TDK) see English language abstract (WPI Acc No: 87-15908/23)	1

SF2(p)



Category	Identity of document and relevant passages	Relevant t claim(s)

### Categories of documents

**X:** Document indicating lack of novelty or of inventive step.

**Y:** Document indicating lack of inventive step if combined with one or more other documents of the same category.

**A:** Document indicating technological background and/or state of the art.

**P:** Document published on or after the declared priority date but before the filing date of the present application.

**E:** Patent document published on or after, but with priority date earlier than, the filing date of the present application.

**&:** Member of the same patent family, corresponding document.

**Databases:** The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).

**THIS PAGE BLANK (USPTO)**